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A METHOD FOR THE DETERMINATION OF α , n , and I_0

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A METHOD FOR THE DETERMINATION OF α , n , and I_0

Interest in electrode reactions having very low chemical polarizations ΔE and in the values of the transfer coefficient α , the number of electrons involved the half reaction n , and the exchange current density I_0 for these reactions has increased. Such interest is pertinent to the investigation of fuel cells and corrosion. A method is presented here for evaluating α , n , and I_0 by applying the general polarization equation for a net cathodic slow discharge rate-controlling reaction* and the two limiting equations to the polarization data obtained experimentally from an electrode reaction.

The general equation can be written in the form,

$$\Delta E = -\frac{RT}{\alpha n \mathcal{F}} \ln I_0 + \frac{RT}{\alpha n \mathcal{F}} \ln \frac{I}{1 - \exp \left(-\frac{n \mathcal{F} \Delta E}{RT} \right)}$$

or in the form of the Tafel equation, where A may be considered a correction to the Tafel equation

$$\Delta E = a + b \log AI \quad (1)$$

where

$$a = -\frac{RT}{\alpha n \mathcal{F}} \ln I_0$$

*S. Glasstone, An Introduction to Electrochemistry, Princeton, N. J., D. Von Nostrand Co., Inc., 1946, p. 460

$$b = \frac{RT}{\alpha n \mathcal{F}}$$

$$A = \frac{1}{1 - \exp\left(-\frac{n \mathcal{F} \Delta E}{RT}\right)}$$

A plot of A versus $n\Delta E$ is presented in Fig 1. When $n\Delta E \geq 0.077$ volt, the error in the Tafel equation is less than 5 percent.

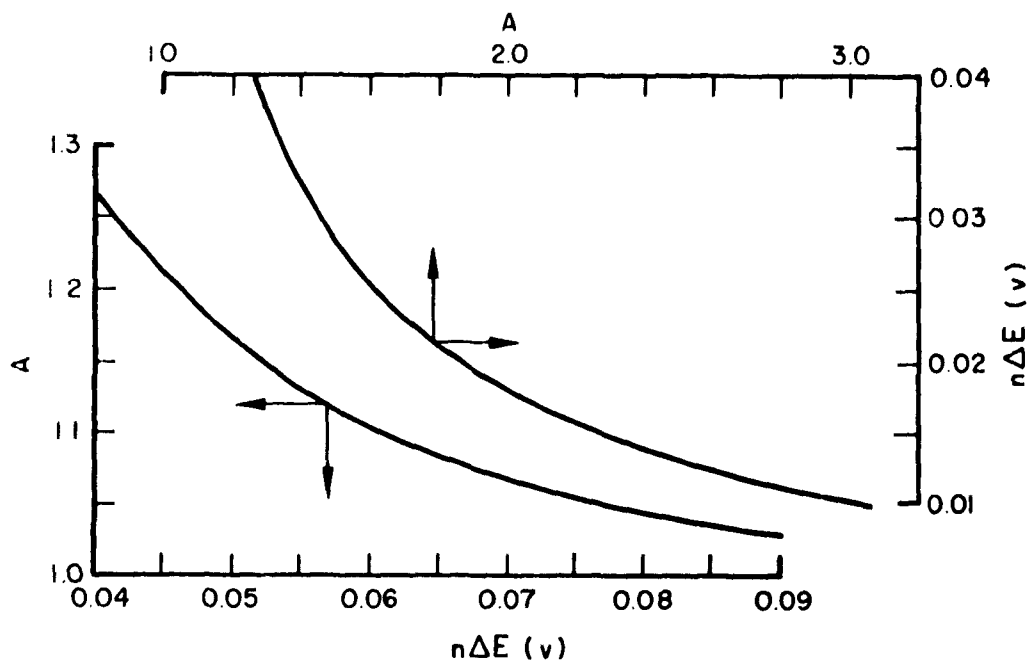


Fig. 1 Correction to be Applied to the Tafel Equation at low Polarizations at 25°C

At low polarizations, the polarization is a linear function of the current density I ,^{*}

$$E = \frac{RT}{n\mathcal{F}} \ln \frac{I}{I_0}$$

This equation has an error of less than 5 percent when $n\Delta E \leq 0.020$ volt ($\alpha = 0.5$).

Application of the Tafel equation, Eq. (1) and the linear equation to the appropriate polarization ranges should lead to a close approximation of the values of α , n , and I_0 for a given electrode reaction. Such application requires that the contributions of resistance and concentration polarization be insignificant over the range in which these equations are applied.

A plot of ΔE versus $\log I$ for large values of ΔE would give the Tafel slope b and the intercept a . A plot of ΔE versus $\log AI$ using different values of n for intermediate values of ΔE would give a family of lines having different slopes. The correct value of n would correspond to the line having the same, or approximate slope as that obtained by using the Tafel equation. It is then possible to calculate α from the value of the Tafel slope b . Using these parameters, the value of I_0 can be calculated from the intercept a . If concentration or resistance polarization becomes significant in the range of applicability of the Tafel equation, incorrect values of the parameters α , n , and I_0 will be obtained.

A further check may be made by making a linear plot of ΔE versus I at low polarizations and by comparing the value of nI_0 obtained from the slope with that calculated at higher polarizations. The value of nI_0 obtained from the linear plot will not agree with that found from the Tafel equation if the contributions of resistance and concentration polarization are significant. In this event, the Tafel equation should not be used. The values of n and I_0 obtained from the family of curves given by Eq. (1) would then be compared with the values of nI_0 obtained from the linear plot. These values of n and I_0 would be used to compute α .

^{*}Ibid, p. 461

An evaluation of the current parameters from a hypothetical experiment is illustrated in Figs. 2 and 3. Currents and polarizations are indicated by the data points. No units are indicated for the current density because they are immaterial to the discussion and affect only the value of the exchange current density. Thus, in any similar treatment the choice of electrode area must be explicit, e.g., the apparent area, the B.E.T. area, or a calculated area based upon some known configuration.

Some limiting effort at a current density of 1000 is indicated in Fig. 2, where above a polarization of about 0.05 volt, the points seem to be in a straight line. This is somewhat below the limit of 0.077 volt, unless $n > 1$. A straight line drawn through these points gives a value of 0.993 for αn and 15.5 for the intercept I_0 .

Choosing a value of $n=1$ and multiplying the experimental current density by the value of A at the particular polarization, the graph of ΔE versus $\log AI$ is plotted. Since this graph is not a straight line, a new value of n must be chosen and the data re-plotted. Choosing $n = 3$ also results in a curved line. However, if $n = 2$ is chosen, the plot is a straight line. Furthermore, this line has a slope such that $\alpha n = 0.993$, and the intercept is 15.5. The curve in the plot of ΔE versus $\log AI$ for low values of n is toward constant (or increasing) current density as ΔE becomes smaller and toward smaller current density for high values of n as ΔE becomes smaller.

A linear plot of the data from the hypothetical experiment is presented in Fig. 2. It should be used only for $n \Delta E \leq 0.020$ volt. The data indicate a falling off above 0.010 volt, with a straight line through the points for $\Delta E < 0.010$ volt. This line has a slope such that $nI_0 = 30.8$. For $n = 2$, only values of $\Delta E < 0.010$ volt can be used for the linear plot.

This hypothetical experiment covers both limiting equations and the general equation. If, for instance, $n = 8$, the linear plot would require data for $\Delta E < 0.002$ volt, and its values might not be too precise. Thus, unless considerable care is exercised, the linear plot will not be accurate enough to use.

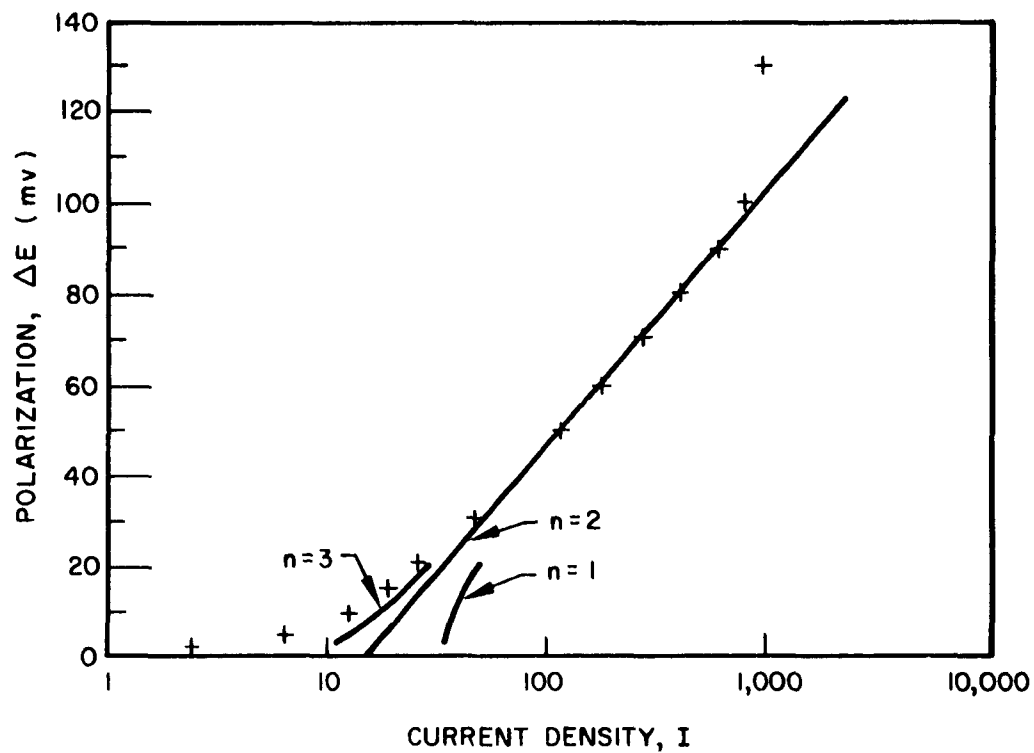


Fig. 2 Determination of the Current Parameters for a Hypothetical Experiment at 25°C: Logarithmic Plot

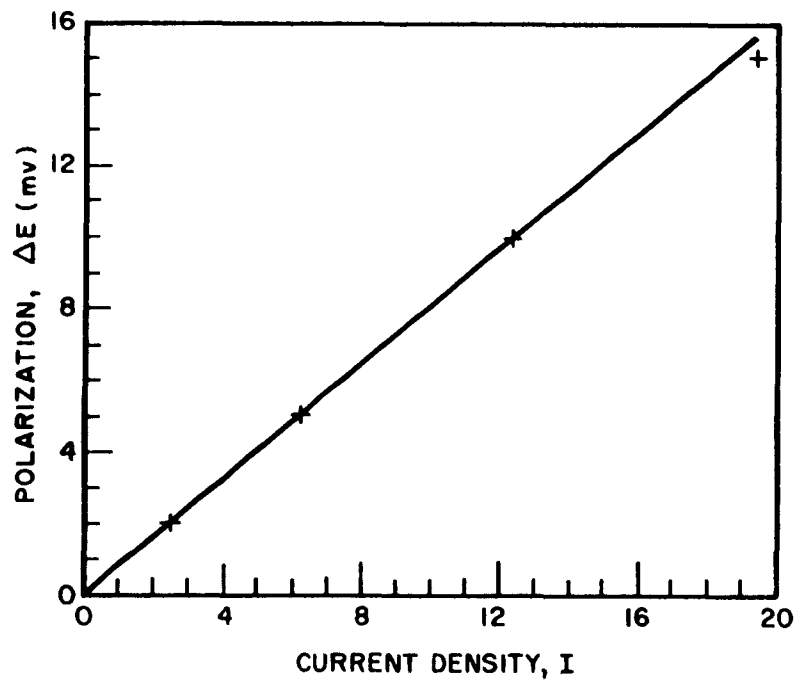


Fig. 3 Determination of the Current Parameters for a Hypothetical Experiment at 25°C: Linear Plot

A limiting effect is indicated at a current density of 1000. If this effect occurred at a current density of 100, or even 200, for the case illustrated in Fig. 2, the linear portion of the data would vanish or be so short that constructing the correct Tafel line would be almost impossible. Thus, correct parameters could not be obtained if only the limiting equations were used.

The linear equation applies for $n\Delta E \leq 0.020$ volt, the Tafel equation applies for $n\Delta E \geq 0.077$ volt, and the general equation covers the whole range. The polarization range, over which these equations apply, is dependent upon the value of n for the particular reaction. Correct values of the current parameters can only be obtained by a proper consideration of the range of applicability of the individual equations. Before any attempt is made to apply the equations outside these ranges, firm experimental or theoretical evidence must be relied upon to justify their use. The numerical values given in this work are based upon an operating temperature of 25°C. Appropriate corrections should be made for any other operating temperatures. For instance, at about 546°C, the linear equation is applicable for $n\Delta E \leq 0.060$ volt and the Tafel equation is applicable for $n\Delta E \geq 0.231$ volt.

Detailed derivations have been presented to explain deviations from the Tafel equation. For instance, Stern and Geary* derived the equation

$$\left(\frac{d\Delta E}{d\bar{I}_x} \right)_{\Delta E \rightarrow 0} = - \left(\frac{d\Delta E}{d\bar{I}_x} \right)_{\Delta E \rightarrow 0} \cdot \frac{\beta_A \beta_C}{2.3 I_o (\beta_A + \beta_C)}$$

*M. Stern and A. L. Geary, J. Electrochem. Soc., Vol. 104, No. 1, 1957, p. 56.

where β_A and β_C are the Tafel slopes of the anodic and cathodic reactions. Stern* applied this equation to the $\text{Fe}^{+++}/\text{Fe}^{++}$ system using two different electrolytes. Comparison with this work yields,

$$\beta_A = \frac{2.3 RT}{(1-\alpha)(n/\nu)j}$$

$$\beta_C = \frac{2.3 RT}{\alpha(n/\nu)j}$$

where ν is the stoichiometric number used by Stern*. In the sulfate solution, Stern obtained $\beta_A = 0.102$ and $\beta_C = 0.123$; when these values are used to solve for α , there results $\alpha = 0.453$. In the nitrate solution, he obtained a $\beta_A = 0.089$ and $\beta_C = 0.123$; when these values are used to solve for α , there results $\alpha = 0.420$. Substitution of n/ν for n in the general equation (and using the absolute value of the current density) would permit the complete description of Stern's results by the use of that equation, where the experimentally determined parameters are α , n/ν , and I_0 .

Bacarella** applied the method of Stern to the measurement of the corrosion rates of zirconium and Zircaloy-2. While the data, as published, do not allow the development of comparative calculations, it would be quite interesting to apply the methods presented here to the original data.

Evans and Koehler*** determined the rates of corrosion of aluminum alloys using the polarization resistance method of Stern and the voltage intercept method (intercept of the plot of the Tafel equation). Their results indicated the two methods were in agreement.

*M. Stern, *J. Electrochem. Soc.*, Vol 104, No. 9, 1957, p. 559

**A. L. Bacarella, *J. Electrochem. Soc.*, Vol 108, No. 4, 1961, p. 331

***S. Evans and E. L. Koehler, *J. Electrochem. Soc.*, Vol 108, 1961, p. 509